

polymer in electrode (Ic?)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



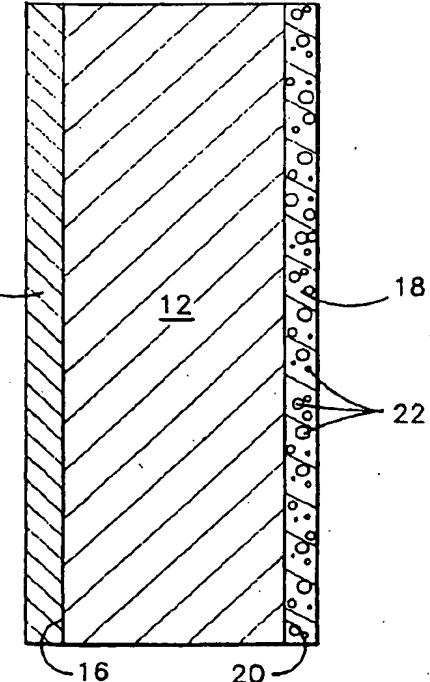
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: H01M 8/10, C25B 9/00	A1	(11) International Publication Number: WO 95/15016 (43) International Publication Date: 1 June 1995 (01.06.95)
(21) International Application Number: PCT/US94/13620		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 29 November 1994 (29.11.94)		
(30) Priority Data: 158,657 29 November 1993 (29.11.93) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant: INTERNATIONAL FUEL CELLS CORPORATION (US/US); 195 Governor's Highway, South Windsor, CT-06074-(US)		
(72) Inventor: BETT, John, A., S.; 10 Meadow Brook Road, Hamden, CT 06517 (US).		
(74) Agent: COHEN, Alan, C.; United Technologies Corporation, Patent Dept. - MS 524, United Technologies Building, Hartford, CT 06101 (US).		

(54) Title: CELL/MEMBRANE AND ELECTRODE ASSEMBLY FOR ELECTROCHEMICAL CELLS

(57) Abstract

The present invention discloses an electrode assembly for use in electrolysis cells in which the catalytic particles (22) forming at least one of the electrodes is in contact with a solid polymer ion exchange material which has a higher equivalent weight than the solid polymer electrolyte membrane (12). Also disclosed is a method for making the electrode assembly.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Description

CELL/MEMBRANE AND ELECTRODE ASSEMBLY FOR ELECTROCHEMICAL CELLS

Technical Field

5 The technical field to which this invention
pertains is an improved electrode assembly for use in
electrolytic cells, in particular an electrode assembly
for use in fuel cells and electrolysis cells and methods
for manufacturing such assembly.

10 Background of the Invention

Proton ion exchange membranes used as solid polymer electrolytes in fuel cells and electrolysis cells have been used for years. The preferred electrolyte membranes are those based on perfluorosulfonic acid and are commercially available as NAFION® from the DuPont de Nemours Company of Delaware. In a typical cell the electrolyte membrane is sandwiched between and in intimate contact with a cathode catalyst and an anode catalyst forming the cathode and anode respectively.

During operation of the cell, reactants are introduced into both the anode and cathode chambers and migrate through the electrodes to the electrolyte membrane/electrode interface where the following half cell reactions take place.



(the direction of the cell reaction is dependent on whether the cell is being operated as a fuel cell or an electrolysis cell.) In either event, one important

2

feature of the electrolyte membrane is that it have the requisite ability to transport the ionic species from one electrode to the other electrode easily. This ability is referred to as the resistivity or conductivity of the electrolyte. Since it is important to transport the ionic species across the electrolyte as easily as possible, it is desirable to have an electrolyte membrane having a high conductivity or low resistivity. It is further known that those electrolyte membranes with high conductivity also have, what is termed, a low equivalent weight. The equivalent weight is defined as the weight of polymer in the dry non-hydrated state) per equivalent of conducting ionic species therein. (For fuel cells and electrolysis cells the current conveying ions are protons.) In other words;

Equivalent Weight = polymer molecular weight/No. of equivalents of current conveying ions.

It is believed that the high concentration of proton ions creates a greater number of pathways for the ionic species generated at one electrode to migrate through the electrolyte to the other electrode where the ionic species is catalyzed in the half cell reaction.

In attempting to improve the cell operation, investigators have focused on two aspects of cell technology. First, developing the conductivity of the electrolyte and secondly, improving the catalyst interface at the electrode surface.

As discussed above, the principle interest in electrolyte membrane technology has been to develop membranes having low equivalent weights which therefore have low cell resistivity.

The problems at the electrolyte/electrode interface are more complex. As an example of these problems, this discussion will focus on the operation of a fuel cell; however, similar problems exist in electrolysis cells.

During the operation of the fuel cell, the hydrogen ions formed at the anode/electrolyte interface migrate through the electrolyte membrane to the cathode catalyst. Once they reach the cathode electrode/electrolyte interface, the hydrogen ions must come in contact with a reactive catalytic site on the cathode electrode where, in the presence of the oxidant, the half cell reaction (2) takes place.

In order for the cathode electrode to operate properly, it must possess certain physical properties. It must be gas permeable to permit the oxidant to pass through it to the electrode/electrolyte interface. It must further be electrically conductive and it must permit easy removal of the product water associated with the reaction. Not all of these properties are consistent with one another in the materials used in the preparation of these electrodes. In the prior art electrodes, the catalyst is mixed with a hydrophobic material (TEFLON[®]), and the mixture is then applied to the surface of the electrolyte membrane and bonded to it through the application of heat and pressure to form the electrode. The theory being that the hydrophobic TEFLO^N, would prevent the retention of product water while acting as a binder for the catalyst. Unfortunately, TEFLO^N is not electrically or ionically conductive. This means that in the event the TEFLO^N surrounds a catalyst particle it would insulate it and remove it as a potential reactive site preventing either electrons or protons from reaching the catalyst particle. Such a result lowers the reactivity and, therefore, the effectiveness of a particular loading of catalyst forming the electrode. This means that in order to compensate for the loss of these reactive sites, and to achieve the desired reactivity for a given electrode, additional catalyst must be loaded onto the electrode. As the preferred catalysts are either noble metal or alloys of noble metals, this adds additional

cost to the manufacture of such devices.

Recently researchers have investigated ways of overcoming the shortcomings of using TEFLOM in order to prepare effective electrodes having lower loading of catalyst. One approach is described in Wilson et al., Thin-film catalyst layers for polymer electrolyte fuel cell electrodes, Jour. of App. Electrochem. 22 (1992) pp 1-7 and Wilson et al., High Performance Catalyzed Membranes of Ultra-low Pt Loadings for Polymer

10 Electrolyte Fuel Cells, J. Electrochem Soc. Vol. 139, No 2, February 1992 (the contents of which are incorporated herein by reference). These articles suggest replacing the TEFLOM of the prior art with particles of electrolyte membrane material (NAFION). Mixing this
15 NAFION material with the catalyst particles and bonding them to the surface of the electrolyte membrane thereby forming the electrode. In effect since the binder material is the same material as the electrolyte it will have the same ionic electrical conductivity as the
20 electrolyte membrane. And although it does not have the hydrophobicity of the TEFLOM, this may be achieved by applying a TEFLOM coated, conductive fabric or paper to the back of the electrode at the opposite face from the electrolyte/electrode interface to deal with the problem
25 of water retention.

Although these advances have improved the operation of these cells, further improvements are necessary to lower the cost of these cells and to improve their efficiency.

30 **Brief Description of the Invention**

The present invention discloses an improved electrode assembly comprising a solid polymer electrolyte membrane positioned between and in contact with a cathode and an anode, wherein the cathode contains catalytic particles in contact with a solid polymer ion exchange material having a higher equivalent

weight than the equivalent weight of the electrolyte membrane.

The present invention further discloses an improved solid polymer electrolyte membrane for use in electrolytic cells (for example fuel cells as well as electrochemical electrolysis cells). The electrolyte comprises an ion exchange membrane material having at least two regions formed of ion exchange polymers, an interior region and an exterior region wherein the exterior region is an ion exchange material having a higher equivalent weight than the ion exchange material of the interior region. And where the exterior region forms at least one surface of the electrolyte membrane.

Also disclosed is an electrode assembly for use in electrolytic cells having an anode catalyst bonded to one surface of the solid polymer electrolyte as described above and a cathode catalyst bonded to the opposite side of the electrolyte from the anode catalyst, where the cathode particles are in intimate contact with the exterior region of the electrolyte membrane.

Still a further feature of the invention is an electrode assembly for use in electrolytic cells in which the cathode electrode is in intimate contact with the surface of the electrolyte membrane of uniform equivalent weight and comprises a mixture of catalytic particles and proton ion exchange material, said proton ion exchange material having a higher equivalent weight than the electrolyte membrane, and having an anode electrode in intimate contact with the opposite surface of the electrolyte membrane from the cathode electrode.

Further disclosed is a method of manufacturing an electrode assembly of the present invention and a electrolytic cell utilizing such an assembly.

Still further, is disclosed a fuel cell utilizing the electrode assembly of the present invention.

Brief Description the Drawings

Figure 1 is a cross-sectional view of the embodiment of an electrode assembly of the present invention.

5 Figure 2 is a graph depicting how the activity for oxygen reduction of a platinum catalyst changes with the concentration of sulfonic acid groups in a solution of trifluoromethane sulfonic acid. And shows similar behavior of platinum catalyst on a NAFION membrane.

10 Figure 3 is a graph depicting the oxygen reduction activity of a platinum catalyst on a NAFION membrane at differing states of hydration (different effective equivalent weights).

Best Mode for Practicing the Invention

15 Referring to Figure 1, the electrode assembly 10 of the present invention comprises an ion exchange polymer electrolyte membrane 12 having an anode electrode 14 on one surface 16 of the electrolyte membrane 12 and a cathode electrode 18 on the surface 20 of the electrolyte membrane 12 opposite the surface 16 on which the anode 14 is affixed, wherein the cathode catalyst particles 22 are in intimate contact with an ion exchange material having a higher equivalent weight than the electrolyte membrane 12.

20 The ion exchange membranes useful as the electrolyte membrane maybe any of the conventional solid polymer membranes used as a solid polymer electrolyte in prior art electrolytic cells. The preferred polymer membranes are proton ion exchange membranes and are 25 members of the NAFION® family of perfluorosulfonic acid polymers manufactured by DuPont de Nemours Company of Delaware. As was discussed above, the equivalent molecular weight of electrolyte membrane is important in selecting a membrane which will have the necessary high 30 conductivity or low resistivity to be useful in the operation of the cell. Membranes having equivalent

molecular weights of between about 800 and about 1200 are preferred and the most preferred membrane is NAFION 117 which has an equivalent molecular weight of 1100.

The materials for forming the anode are also conventional and would be manufactured and bonded to the electrolyte membrane in conventional manner. Typically, this would comprise forming a mixture of anode catalytic particles and a binder (typically TEFLON®) and then applying this mixture or paste onto the surface of the electrolyte and then bonding and forming the anode through the application of heat and pressure.

The cathode electrode for use in the electrode assembly may be formed by forming a mixture or suspension of catalytic particles at the desired loading with particles of a proton ion exchange polymer material which acts as a binder where the polymer has an equivalent molecular weight higher than that of the electrolyte membrane. This ion exchange material may be a perfluorosulfonic acid type material such as NAFION 117 or other material which is either based on the same base polymer as that of the electrolyte membrane or a different polymer while the catalytic particles may be those conventional catalyst materials used in this art. The key feature in selecting the ion exchange polymer material is that it has an equivalent molecular weight greater than that of the electrolyte membrane. The mixture or suspension is then applied to the surface of the electrolyte membrane in a uniform thickness and through the application of heat and pressure caused to bond to the surface of the electrolyte membrane. The concentration of polymer to catalyst material will vary depending on the materials used and the cell design, however, it is believed that concentrations of about 20 wt % to about 40 wt % polymer to catalyst be preferred, and is preferably substantially uniformly distributed throughout the ion exchange material.

In forming the cathode electrode on the surface of

the electrolyte membrane, it is desirable to make the cathode electrode at least coextensive with the electrolyte surface which is to come in contact with the oxidizing material. This will permit optimum reactivity for the electrode assembly as the higher reactivity for the cathode catalyst, due to its contact with the exterior region of the electrolyte membrane, will be at its maximum.

Alternate manufacturing approaches would be to cast a mixture or suspension of the high equivalent weight material and the catalyst particles onto a non-bonding surface to form a smooth, uniform thickness film. Cause the film to dry and then remove the film from the surface and place it in contact with the surface of the electrolyte. Then bond the film to the electrolyte surface through heat and pressure.

Naturally, it is contemplated that either an anode electrode or a cathode electrode may be prepared by any of these processes.

A further variation for manufacturing such electrodes, would be to prepare a suspension or mixture of the ion exchange polymer of a higher equivalent weight than the electrolyte membrane material together with the desired catalytic particles and paint or spray the suspension or mixture onto the surface of the electrolyte material to a desired thickness. Then drying the suspension and bonding the electrode through the application of heat and pressure.

An alternate approach to manufacturing the electrode assemblies of the present invention would be to prepare an ion exchange electrolyte membrane useful in practicing this invention is comprised of two regions formed of ion exchange polymers having different equivalent weights. The electrolyte membrane would have an interior region and an exterior region where the interior region is comprised of an ion exchange electrolyte material having a lower equivalent weight

than the exterior region and where the exterior region forms at least one of the major surfaces of electrolyte membrane to which at least one of the electrodes is bonded, preferably the cathode.

5 The ion exchange membrane used to form both the exterior region and the interior region of the electrolyte could be the same polymer family as described above for the electrolyte membrane i.e. a member of the perfluorosulfonic family. However, the
10 polymer selected for the exterior region must have a higher equivalent weight than that of the interior electrolyte membrane. In the case where the preferred electrolyte, NAFION 117, is used as the interior membrane, the exterior membrane would have an equivalent weight greater than 1100. However, other ion exchange
15 polymers which would operate as electrolytes in these electrolytic processes and which have equivalent weights greater than that of the interior electrolyte membrane would also be useful.

20 The thickness of the overall electrolyte membrane will be conventional for electrolysis cells which is typically about 2 mils to about 10 mils. The thickness of the exterior region will be about the same thickness as the prior art bonded cathodes used in solid polymer electrolyte electrolysis cells. Typically, this will be about 0.5 mils to about 2 mils. However, the design criteria for selecting a particular membrane will vary with a particular cell design or electrolyte used and are known to those skilled in this art.

25 As in the previous method of forming the electrolyte assembly, it is desirable to make the electrode at least coextensive with the surface of the electrolyte to be exposed to the oxidizing fluid.

30 Such exterior regions having the higher equivalent weight than the interior electrolyte may be formed in a number of ways. One method is to bond a layer of a first ion exchange membrane onto the surface of a second ion

exchange membrane where the first ion exchange membrane has an equivalent weight higher than that of the second ion exchange membrane and the first ion exchange membrane forms the exterior region of the electrolyte membrane. This could be achieved by merely selecting the desired electrolyte membranes, at the predetermined thickness, forming a layer with the two membranes and then bonding them to form a unitary electrolyte. It is contemplated that the laminate bonding could be achieved through the application of pressure and heat, the parameters of which would be the same as those used to bond the electrodes to the surfaces of the electrolyte of the prior art.

In this format, the formation of the anode and the cathode onto the electrolyte to form the electrode assembly would be performed using conventional techniques. This would include applying catalyst particles to opposite surfaces of the electrolyte membrane (the cathode catalyst being deposited onto the surface of the exterior region of the electrolyte membrane) and formed into anode and cathode electrodes through the application of heat and pressure. The respective loadings of catalyst to form the anode and cathode may be conventional; however, it is contemplated that in view of the improved reactivity of the cathode catalyst in contact with the exterior region of the electrolyte membrane, less catalytic material will be needed to achieve the same cell performance.

It is believed that by creating the electrodes with the catalyst material in intimate contact with the high equivalent weight polymer that improved catalytic activity will result. This is based on results of certain experiments which reveal that the oxidation reduction activity of platinum catalysts is increased as the concentration of acid anion groups and accompanying proton ions is decreased within the polymer material.

Such a relationship may be deduced from the results

of the experiments shown in the Figures. In Figure 2, the oxygen reduction activity of platinum was plotted against the concentration of acid groups, in this case sulfonic acid groups, in a solution of liquid trifluoromethane. As is self-evident from the graph, the oxygen reduction activity of the catalyst is inversely proportional to the concentration of sulfonic acid groups. What is additionally noteworthy about this finding is that the oxygen reduction activity of a conventional electrolyte membrane formed of NAFION 117, having an equivalent weight of 1100, with a platinum catalyst bonded to opposite surfaces to act as an anode and cathode, has the same oxygen reactivity at the same concentration of sulfonic acid groups in the membrane as in the liquid solution, confirming the results of the liquid experience.

Further evidence of the relationship between the concentration of acid groups in the membrane material and the oxygen reactivity of the catalyst is demonstrated in Figure 3, in which the effective concentration of acid groups is varied through hydration or dehydration of the membrane. In essence, this simulates how the equivalent weight of a polymer would affect the oxygen reduction activity of the catalyst if one assumes that the equivalent weight is directly proportional to the concentration of acid groups. In this graph, an electrolyte membrane formed of NAFION 117 and platinum electrodes was operated in a fuel cell in which the relative humidity of the fuel (hydrogen gas) was varied during operation. It is believed that as the humidity of the fuel is varied, the hydration of the membrane varies, which in turn varies the effective concentration of the acid groups in the polymer. As can be seen, the greater the hydration the lower the oxygen reactivity of the cell. In each of these experiments, it is clear that the higher the equivalent molecular weight the greater the oxygen reactivity.

The resulting electrode assembly would then be placed in a conventional fuel cell or electrolysis cell assembly to form the fuel cell or electrolysis cell having improved properties. Such a cell would have a porous hydrophobic paper positioned in contact with the surface of the cathode opposite the cathode/electrolyte interface, means for supplying a fuel to the anode and an oxidant to the cathode, all of which are known and conventional. Such an electrolytic cell would have improved oxidation reactivity of the cathode electrode without any meaningful loss of cell conductivity. This will result in higher performance from the cell.

By creating electrode assemblies of the present invention, the efficiency of the devices in which they operate will be enhanced as the activity of the catalysts will be improved while maintaining the high specific conductance of the electrolyte.

CLAIMS

1. An improved fuel cell electrode assembly comprising a solid polymer electrolyte membrane positioned between and in contact with an anode and a cathode where said cathode contains a catalytic material which is in contact with a solid polymer ion exchange material having a higher equivalent weight than the electrolyte membrane.
2. The electrode assembly of claim 1 wherein the cathode catalytic material is dispersed substantially uniformly throughout the ion exchange material.
3. The electrode assembly of claim 1, wherein the solid polymer ion exchange material is in the form of a layer having a thickness of about 2 mils to about 10 mils.
4. An electrode assembly for use in fuel cells, said electrode assembly comprising a ion exchange solid polymer electrolyte, positioned between and in contact with an anode electrode and a cathode electrode wherein said electrolyte comprises an interior region and an exterior region in which the ion exchange solid polymer electrolyte of said exterior region has a higher equivalent weight than the ion exchange solid polymer electrolyte of the interior region and said cathode is in intimate contact with said exterior region.
5. The electrolyte of claim 4 wherein the ion exchange polymer of the interior and exterior regions is a perfluorosulfonic acid.
6. An electrode assembly for use in electrochemical fuel cells or electrochemical electrolysis cells said electrode assembly having a solid polymer electrolyte membrane having two surfaces wherein on one surface is

5. bonded a catalytic material to form the cathode where a cathode catalyst is in contact with an ion exchange material having a higher equivalent weight than the electrolyte membrane.
7. The electrode assembly of claim 6 wherein the catalytic material of the cathode is substantially uniformly dispersed in the ion exchange polymer having a higher equivalent weight than the polymer electrolyte.
8. A method of making an electrolyte assembly having uses in a electrolytic cell comprising a solid polymer electrolyte membrane having, on opposite sides of said electrolyte membrane, an anode and a cathode each in intimate contact with the surface of the electrolyte comprising
 - 5 forming a mixture of the cathode catalyst and particles of a solid polymer ion exchange material having an equivalent weight higher than that of the solid polymer electrolyte;
 - 10 curing the mixture of the catalyst and the ion exchange material to form a cathode;
 - 15 applying the cathode to the opposite surface of the solid polymer electrolyte from the anode and applying sufficient pressure and heat to cause the cathode to bond to the surface of the solid polymer electrolyte.
9. The method of claim 8 wherein the cathode for both surfaces are applied and pressure bonded simultaneously.
10. A method of making an electrolyte assembly having uses in electrolytic cells comprising a solid polymer electrolyte membrane having, on opposite sides of said electrolyte membrane, an anode catalyst and a cathode catalyst in intimate contact with the surface of the electrolyte comprising
 - 5

applying a layer of ion exchange material to at least one surface of a solid polymer electrolyte wherein the equivalent weight of the ion exchange material is greater than that of the solid polymer electrolyte,

bonding said ion exchange material to the surface of the solid polymer electrolyte membrane,

applying a catalytic material to the surface of the ion exchange material bonded to the solid polymer electrolyte; and

applying sufficient heat and pressure to cause the catalytic material to be embedded into the layer of ion exchange material thereby forming the cathode electrode; and

applying a second catalytic material to the opposite surface of the solid polymer electrolyte; and

applying sufficient pressure and heat to cause the catalytic material to be embedded into the surface of the solid polymer electrolyte and thereby forming the anode.

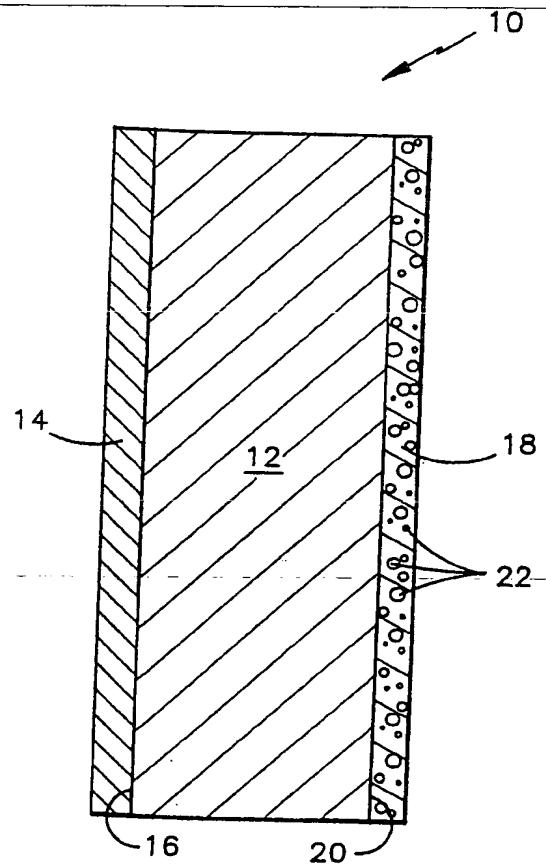
11. The method of claim 10 wherein the anode and cathode are bonded simultaneously.

12. The method of claim 10 wherein the catalysts for the anode and the cathode are different.

13. A fuel cell comprising a solid polymer electrolyte membrane, having an anode and cathode positioned on opposite surfaces of the electrolyte where catalytic particles are in intimate contact with an ion exchange polymer having a higher equivalent weight than the electrolyte membrane.

14. The fuel cell of claim 13 wherein the catalytic particles are substantially uniformly dispersed throughout the ion exchange polymer forming the cathode.

1/2

fig. 1

2/2

fig.2

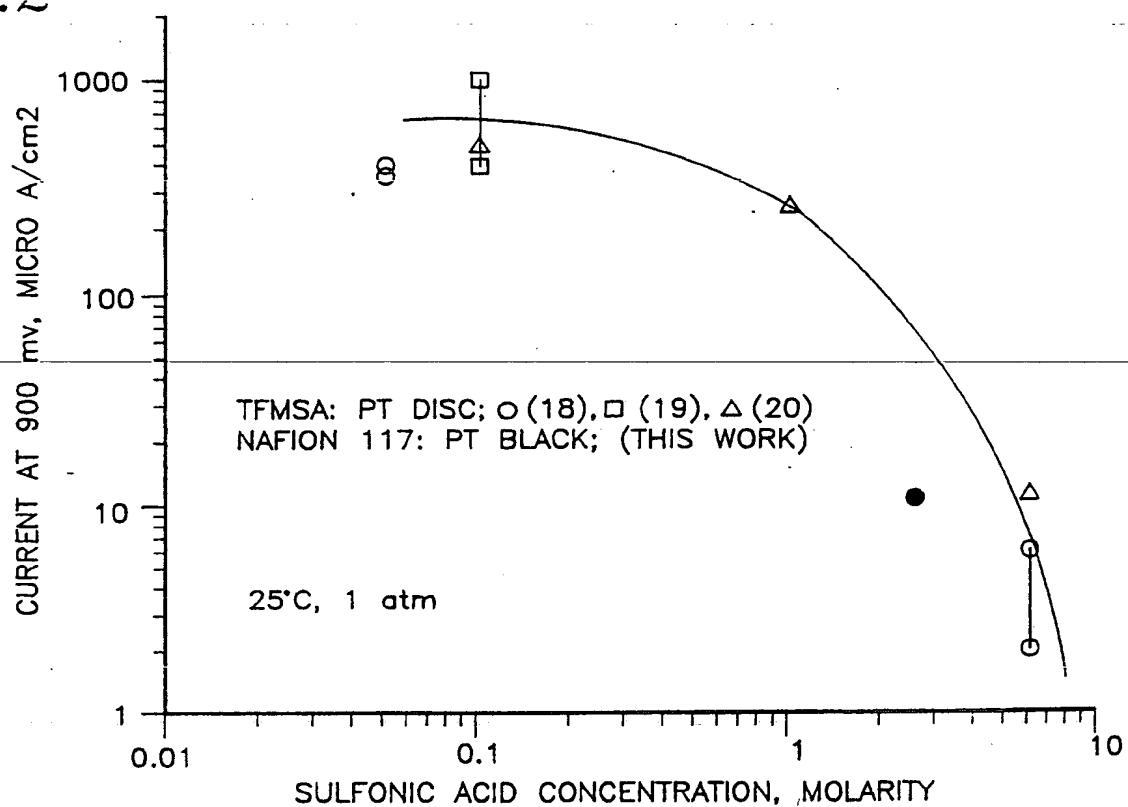
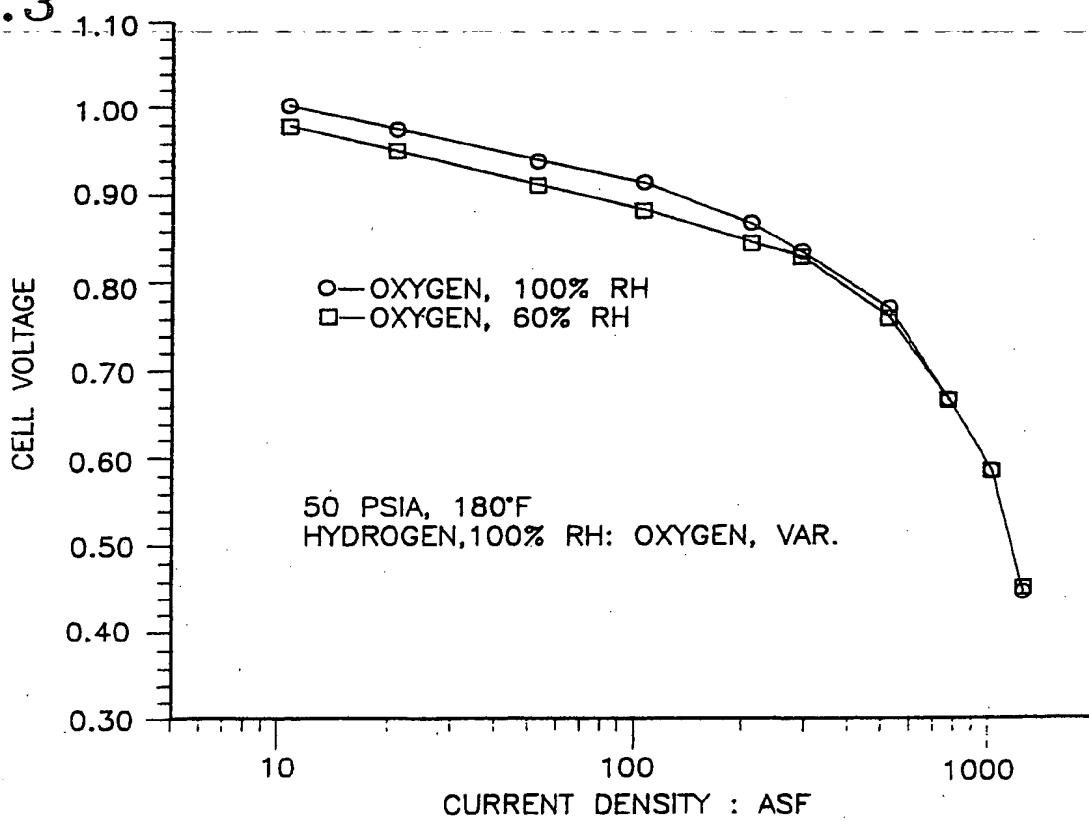


fig.3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/13620

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M8/10 C25B9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
1 X	JOURNAL OF POWER SOURCES, vol. 36, no. 3, 1 December 1991 LAUSANNE CH, pages 299-320, SUPRAMANIAM SRINIVASAN ET AL 'High energy efficiency and high power density proton exchange membrane fuel cells - electrode kinetics and mass transport' see page 306 see page 311, last paragraph see page 302, paragraph 1 see page 301, paragraph 2 --- -/-	1,2,6,7, 13,14
A		8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

2

Date of the actual completion of the international search 29 March 1995	Date of mailing of the international search report 10.04.95
--	--

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 cpo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

D'hondt, J

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/13620

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
1 X	ELECTROCHIMICA ACTA, vol. 38,no. 12, 1993 OXFORD GB, pages 1661-1669, SANJEEV MUKERJEE ET AL 'EFFECT OF SPUTTERED FILM OF PLATINUM ON LOW PLATINUM LOADING ELECTRODES ON ELECTRODE KINETICS OF OXYGEN REDUCTION IN PROTON EXCHANGE MEMBRANE FUEL CELLS' see page 1663, left column, paragraph 2 ---	1,2,6,7, 13,14
1 X	PROCEEDINGS OF THE 28TH INTERSOCIETY ENERGY CONVERSION ENGINEERING CONFERENCE IECEC-93 8-13 AUGUST 1993, vol. 1, GEORGIA, pages 1.1195-1.1201, SUPRAMANIAM SRINIVASAN ET AL 'Progress in Proton Exchange Membrane fuel Cell Technology at Texas A&M University' see page 1.1196, left column; table 1 ---	1,2,6,7, 13,14
1 X	PROCEEDINGS OF THE 28TH INTERSOCIETY ENERGY CONVERSION ENGINEERING CONFERENCE IECEC-93 AUGUST 8-13, vol. 1, August 1993 GEORGIA, pages 1.1227-1.1232, LARRY SWETTE ET AL 'Development of Single-Unit Acid and Alkaline Regenerative Solid Ionomer Fuel Cells' see page 1.1229, right column, last paragraph ---	10
2 A	PROGRESS IN BATTERIES AND SOLAR CELLS, vol. 8,no. 1, 1989 CLEVELAND US, pages 302-305, J.R. HUFF 'THE ION EXCHANGE MEMBRANE ELECTROLYTE FUEL CELL' see page 303, paragraph 2; table I ---	1
1 P,X	EP,A,0 577 291 (JOHNSON MATTHEY PLC) 5 January 1994 see column 10, line 16 - line 42 see column 10, line 54 - column 11, line 2 ---	1,2,8,9, 13,14
1 A	WO,A,92 15121 (US ENERGY) 3 September 1992 see page 8, line 14 - page 9, line 10; claims 5-7 see page 14, line 32 - page 15, line 14 ---	1,8,9
8 X	US,A,4 272 560 (BACZEK STANLEY K ET AL) 9 June 1981 see column 8, line 31 - line 35 ---	6
8 X	FR,A,2 519 030 (GEN ELECTRIC) 1 July 1983 see example 4 ---	6

-/-

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/13620

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 009 788 (GEN ELECTRIC) 20 June 1979 see page 4, line 43 - line 50 -----	6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US 94/13620

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0577291	05-01-94	AU-B-	4137293	23-12-93
		CA-A-	2098800	21-12-93
		JP-A-	6052862	25-02-94
WO-A-9215121	03-09-92	US-A-	5234777	10-08-93
		EP-A-	0600888	15-06-94
		US-A-	5211984	18-05-93
US-A-4272560	09-06-81	NONE		
FR-A-2519030	01-07-83	US-A-	4749452	07-06-88
		US-A-	4832805	23-05-89
		AT-B-	382397	25-02-87
		AT-B-	376709	27-12-84
		AU-B-	566067	08-10-87
		AU-A-	9191682	07-07-83
		BE-A-	895510	29-06-83
		DE-A,C	3247665	07-07-83
		GB-A,B	2113251	03-08-83
		JP-B-	6031457	27-04-94
		JP-A-	58144488	27-08-83
		NL-A-	8205018	18-07-83
		SE-A-	8207485	01-07-83
GB-A-2009788	20-06-79	US-A-	4210501	01-07-80
		US-A-	4224121	23-09-80
		AU-B-	519593	10-12-81
		AU-A-	4239378	14-06-79
		AU-B-	518335	24-09-81
		AU-A-	4239478	28-06-79
		BE-A-	872632	08-06-79
		BE-A-	872634	08-06-79
		CA-A-	1152451	23-08-83
		CA-A-	1125697	15-06-82
		CH-A-	645552	15-10-84
		CH-A-	650032	28-06-85
		DE-A-	2844495	13-06-79
		DE-A-	2844499	13-06-79
		DE-C-	2857627	30-12-82
		FR-A,B	2411029	06-07-79

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US 94/13620

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2009788		FR-A, B 2411248	06-07-79
		GB-A, B 2009792	20-06-79
		GB-A, B 2071157	16-09-81
		JP-A- 59064789	12-04-84
		JP-C- 1285250	09-10-85
		JP-A- 54093690	24-07-79
		JP-B- 58054611	06-12-83
		JP-C- 1370075	25-03-87
		JP-A- 54095996	28-07-79
		JP-B- 61027472	25-06-86
		NL-A- 7811995	12-06-79
		NL-A- 7811996	12-06-79
		SE-B- 453518	08-02-88
		SE-A- 7812639	02-08-79
		SE-A- 7812641	10-06-79
		AU-B- 518219	17-09-81
		AU-A- 4239178	28-06-79
		BE-A- 872633	08-06-79
		CA-A- 1137022	07-12-82
		CH-A- 650031	28-06-85
		DE-A- 2844496	13-06-79
		FR-A, B 2411249	06-07-79
		GB-A, B 2009795	20-06-79
		JP-C- 1389151	14-07-87
		JP-A- 54112398	03-09-79
		JP-B- 61006156	24-02-86
		JP-A- 58181879	24-10-83
		NL-A- 7811997	12-06-79
		SE-B- 453602	15-02-88
		SE-A- 7812640	02-08-79
		SU-A- 1584752	07-08-90
		US-A- 4956061	11-09-90
		US-A- 4569735	11-02-86
		JP-C- 1370146	25-03-87